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Insight into the Synergistic Effect on Selective Adsorption for Heavy Metal Ions by a Polypyrrole/TiO2Composite

Abstract

Polymer/metal oxide composites are promising candidates for the treatment of water pollution. Adsorption selectivity as well as a large adsorption capacity are two key factors for treating wastewater containing multiple ions. Herein, a PPy+/TiO2(O-) composite with a heterojunction structure was first discovered to have novel selectivity toward heavy metal ions. An interesting self-doping nature of TiO2(O-) together with SO42-for PPy+was reported. This interesting structure contributed to an impressive selective adsorption capability with an ascending order of Zn2+> Pb2+≫ Cu2+in a ternary ion system, where the adsorption for Cu2+could be almost suppressed. Through the designed adsorption experiments and characterization techniques including Fourier transform infrared, thermogravimetric analysis, and X-ray photoelectron spectroscopy, a universal synergistic mechanism for PPy+/TiO2(O-) composite was first proposed and confirmed. The doping and dedoping of metal oxide (dopant) from the polymer dictates the adsorption selectivity, where the selectivity is determined by the interaction between TiO2and heavy metal ions. This work may provide some useful guidelines for designing adsorbents with selectivity toward specific heavy metal ions.

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Insight into the synergistic effect on selective adsorption for heavy metal ions by a polypyrrole/TiO_2 composite

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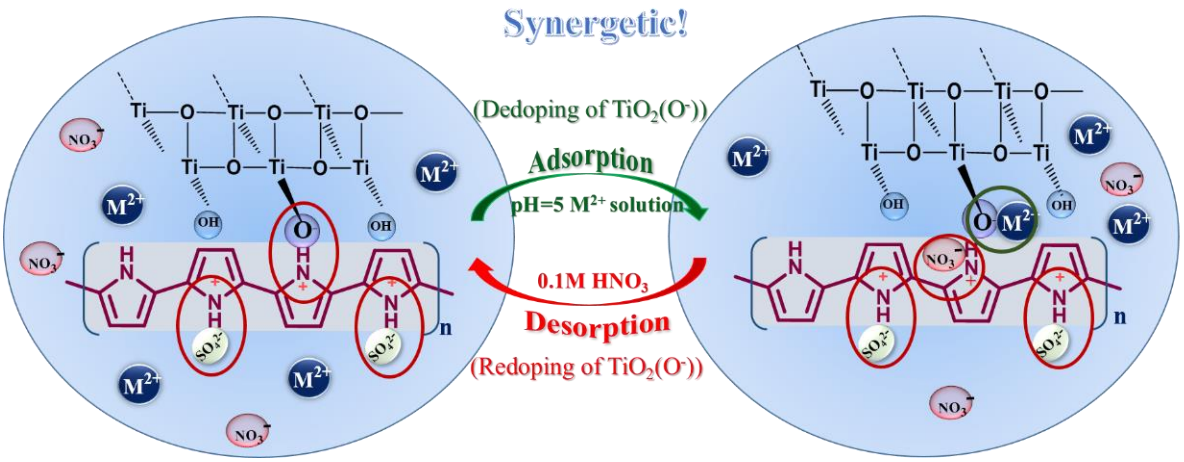


Abstract

Polymer/metal oxide composites are prime candidates for the treatment of water pollution. For this purpose, it is key that the composite has adsorption selectivity, as well as a large adsorption capacity, which is especially important for wastewater containing multiple ions. Herein, a $PPy^{+}/TiO_2(O^{-})$ composite with a heterojunction structure was first discovered to have novel selectivity towards heavy metal ions. An interesting self-doping nature of $TiO_2(O^{-})$ together with SO_4^{2-} for PPy^{+} was reported. This interesting structure contributed to an impressive selective adsorption capability with an ascending order of $Zn^{2+}>Pb^{2+}>>Cu^{2+}$ in a ternary ion system, where the adsorption for Cu^{2+} could be almost suppressed. Through the designed adsorption experiments and characterization including FTIR, TGA and XPS, a universal synergistic mechanism for the polymer/metal oxide composite was first proposed and confirmed. We suggest that the doping and dedoping of the metal oxide (dopant) from the polymer dictates the special adsorption selectivity of the composite, where the selectivity is determined by the interaction between TiO_2 and heavy metal ions. This mechanism we proposed may provide some guidelines for designing adsorbents with selectivity towards specific heavy metal ions.

1. Introduction

Water pollution with heavy metal ions produced from the industry of mining, painting, car radiator manufacturing, batteries, and metal plating etc. is increasingly becoming a significant environmental problem [1]. Adsorption is regarded as a prospective treatment for heavy metal ions due to its low cost, simplicity and easy operational conditions, attracting wide attention from academic and industrial areas[2-4]. However, several kinds of heavy metal ions can co-exist in natural and industrial water environments. These ions compete for adsorption sites, leading to a decreased adsorption capacity [3, 5].

Therefore, in addition to having a large adsorption capacity, we have been concerned about the selective adsorption ability of the adsorbent, which is especially important in the treatment of wastewater.

Another important aspect to consider is synergistic phenomena, which can be found everywhere, from physics to chemistry. Many interesting properties such as solubility and hydrophilicity of a composite can also be introduced by the synergistic properties of the combined material [6-10]. Thus, the design and application of polymer/metal oxide composite have increasingly been the subject of investigation in recent years due to their interesting synergistic effect between polymer and metal oxide [6-11]. J. Yang et al.[11] synthesized a lignosulfonate-graphene oxide-polyaniline (LS-GO-PANi) nanocomposite for Pb(II) adsorption, and deduced that the synergistic phenomena between PANi and LS-GO may play a key role in the adsorption. J.Y. Huang et al.[7] prepared polyimide (PI)/silica powders for heavy metal ion removal. The synergistic effect between silica and polyimide lead to the improvement of the adsorption capacity and affinity. Even though composite synthesis for adsorption purposes is a subject undergoing intense study, the mechanism of the synergistic effects in these studies was only inferred without detailed investigation. The exact mechanism is still unknown. It is important to determine a universal mechanism for the synergistic effects to provide a guideline to design an adsorbent with improved adsorption capacity. Therefore, a detailed investigation on the synergistic effect of a composite should be extensively conducted.

To solve this problem, PPy and TiO_2 were selected for the study of synergistic effects. Specifically, the conjugated polymer polypyrrole (PPy) is a promising candidate due to its novel conjugated structure

and redox properties, offering a rich electrochemical chain that undergoes ion doping and dedoping on the pyrrolylium nitrogen (Scheme ***S*1**), which may additionally experience interaction and synergistic effect with metal oxides[12-16]. Metal oxides have demonstrated a selective adsorption affinity to some heavy metal ions such as Mn oxides toward Cu(II), Fe oxides to Pb(II), while Zn(II) can be specifically attracted by Si oxides[17]. This could lead to synergistic effects between PPy and metal oxides and is expected to produce a material with selective ion-uptake. Even though there has been some published literature concerning PPy/metal oxides for heavy metal adsorption [18-21], there have been limited reports on adsorption in multiple metal ions solutions to take the selectivity of adsorption into consideration.

Herein, the overall aim of this paper is to gain insight into the synergistic mechanism between polymer and metal oxide for the selective adsorption of metal ions. The redox states, structure, textural properties and interaction between PPy and TiO_2 were carefully characterized. Various adsorption experiments, including kinetic, single and multi-component isotherms, were designed and conducted to reveal the individual and competitive adsorption properties for Pb(II), Zn(II) and Cu(II). Finally, the mechanism of the synergistic effect between PPy and $TiO_2$was first proposed and supported by pH experiments, as well as technical instruments including FT-IR, TGA and XPS. The novelty of this work is obtaining a new discovery and a general understanding of a mechanism for the synergetic effect between a polymer and metal oxide and on the selective adsorption of heavy metal ions for the removal of pollutants from waste water. The mechanism proposed may be of great value in aiding the design of adsorbents with selectivity towards certain heavy metal ions.

2. Experimental

2.1 Materials

The chemicals used in this study were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. Pyrrole was distilled twice and stored in the dark prior to use. The standard heavy metal solutions were prepared from $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, respectively with deionized water.

2.2 Synthesis of the PPy, TiO_2 and PPy/TiO_2 composite

The PPy/TiO_2 composite doped with H_2SO_4 was synthesized using in-situ chemical oxidative polymerization[22]. The TiO_2 was prepared through sol-gel method. The volume ratio of 5:2 of n-propanol and tetrabutyl titanate were carefully charged into 200 mL, 0.24 mol/L of H_2SO_4 solution and stirred for 24 h. The formed TiO_2 suspension solution was subsequently cooled to 5 °C in the dark before 0.675 mL of pyrrole monomer was added. Then 25 mL, 1.0 mol/L of $FeCl_3$ solution was dosed dropwise to the solution and stirred for another 24 h in dark. Finally, the obtained dark composite was filtrated and washed with 0.01 mol/L H_2SO_4 solution several times to remove the oligomer and other impurities. For comparison, pure TiO_2 was prepared using the same procedure but without adding pyrrole monomer and $FeCl_3$; pure PPy was synthesized using the same procedure but without adding TiO_2.

2.3 Characterization

The Fourier transform infrared spectra (FT-IR) of PPy, TiO_2 and the PPy/TiO_2 composite were performed on a BRUKER TENSOR 37 FT-IR spectrometer by the KBr pellet method over a range of 4000-400 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) spectra were determined on a Kratos Axis Ultra DLD, with an Al monochromatic X-ray source (1486.71 eV). All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. The zeta potential investigations were conducted on a Malvern Zetasizer Nano ZS90. The thermogravimetric (TG) analysis was investigated

on a Setaram Labsys Evo in N_2 flow, and the heating rate was 10°C/min. X-ray diffraction (XRD) patterns were acquired on an X'Pert PRO Diffractometer with wavelength of 1.5406Å (Cu-Kα radiation method) over a range of 10-80 degrees. The N_2 adsorption and desorption isotherms were recorded on a Builder SSA-4200 at 77K and the specific surface area, total pore volume and average pore radius were calculated using a Builder analysis software. Scanning electron microscopy (SEM) was performed on a JSM-6700F. Transmission electron microscopy images (TEM) were recorded on a JEM model 2100 electron microscope. The concentrations of heavy metal ions were determined using an inductive coupled plasma emission spectrometer (ICPE-9000, Shimadzu).

2.4 Adsorption experiments

In all adsorption experiments, the dose of adsorbent was 2 g/L, and the volume of heavy metal solution was 20 mL. All experiments were conducted in a shaker at a constant temperature, and the agitation speed was kept at 200 rpm. To avoid the influence of precipitation of metal ions on the adsorption, the solution pH was kept at 5.

In the kinetic experiment, the composite was dosed in 400 mg/L Pb^{2+}, Zn^{2+} and Cu^{2+} solutions, respectively, with various contact times (0-180 min). In the single ion isotherm investigations, the composite was dosed in the Pb^{2+}, Zn^{2+} and Cu^{2+} solutions with various initial concentration at 15, 25, 45°C, respectively for 3h. For Pb^{2+} adsorption, the initial concentration was 100, 200, 300, 400, 600, 800 mg/L, respectively; while for Zn^{2+} and Cu^{2+}adsorption, the initial concentration was 10, 50, 100, 200, 400, 600 mg/L, respectively. In the multiple ion isotherm investigations, the composite was dosed in the Pb^{2+}, Zn^{2+} and Cu^{2+} mixed solution with initial concentration of 50, 100, 200, 300, 400 mg/L, respectively at 25°C for 3h. In the pH experiment, the experiment was conducted in the solutions with

initial pH from 1 to 5, respectively with an initial heavy metal ion concentration of 200 mg/L for 3h. The pH used was adjusted using HNO_3 and NaOH solution concentrated *(Caution! The HNO_3 and NaOH solutions are highly corrosive!)*.

The adsorption capacity and recycle efficiency was calculated as follows:

$$Q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

$$\text{Recycle efficiency} = \frac{Q_{e,n}}{Q_{e,0}} \times 100\ \% \quad (2)$$

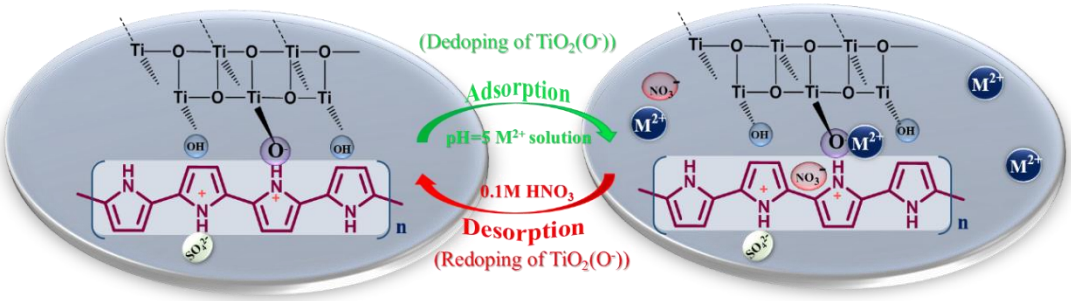
where Q_e (mg/g) is the equilibrium adsorption capacity; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of heavy metal ions, respectively; m (g) is the weight of adsorbent; V (L) is the solution volume; $Q_{e,n}$ represents the adsorption capacity at n cycle, while $Q_{e,0}$ represents the adsorption capacity before the recycle.

3. Results and discussion

3.1. Characterization

The structure of PPy/TiO_2 composite was illuminated by the FT-IR spectra shown in Fig.***S*1**, and the main characteristic bands were listed in Table ***S*1**. For comparison, the spectra of TiO_2 and PPy were also obtained. TiO_2 shows only two broad peaks at 3419 and 400-700 cm^{-1}. After being coated with PPy, the spectrum of the composite clearly exhibits the combination of the typical characteristic peaks assigned to PPy (1551, 1457, 1317 and 1056 cm^{-1}) and TiO_2 (400-700 cm^{-1}), evidencing the successful synthesis of the PPy/TiO_2 composite. In addition, the presence of a strong peak situated at 1056 cm^{-1} which was ascribed to C_β-H suggests an α-α linking and regular polymerization of PPy [16]. Another dopant ion SO_4^{2-} was also detected. However, it is noticeable that the peaks assigned to hydroxyl at 3419 and 1629 cm^{-1} in the spectrum of TiO_2 and those for Py ring(1524, 1442, 1284 and 1025 cm^{-1}) in

the spectrum of PPy shift to lower or higher wavenumbers, confirming the conclusion from the DFT calculations[23] that PPy is p-type semiconducting polymer, which donates its electron cloud density to TiO_2, making TiO_2 to be an n-type material in the PPy/TiO_2 composite. Therefore, following the DFT and the FT-IR results from PPy/TiO_2 composite, we proposed for the first time that TiO_2 should be a dopant, acting through the hydroxyl to dope and undergo charge-transfer (CT) interactions with PPy in the PPy/TiO_2 system. The CT interaction model between PPy and TiO_2 proposed herein (Scheme **1**) may well explain the mechanism of the synergistic adsorption between PPy and TiO_2 and the selective adsorption for heavy metal ions discussed in the later sections.



Scheme **1** The synergistic adsorption between PPy and TiO_2 in the PPy/TiO_2 composite for the selective adsorption for heavy metal ions.

The N 1s XPS spectra shown in Fig.**1** also confirm the PPy p-type doping state ($PPy^+(X^-)$). It can be clearly deconvoluted into two peaks, which reveals the presence of a secondary component at 401.3 eV attributed to the positively charged nitrogen (-N^+-) and a major component at 399.9 eV for the pyrrolylium nitrogen (-NH-)[16]. It also verified that PPy was completely in its oxidation state. In addition, the proportion of positively charged nitrogen in the composite is calculated to be 31.2% according to the peak area, suggesting that almost 31.2% of the PPy are doped [16]. This doping feature is also confirmed by zeta-potential investigation (Fig. **2**). The pH of zero point charge (pH_{pzpc}) of the

composite was 10.3, relatively close to that of PPy (10.4), indicating the positively charged nature of the pyrrolylium nitrogen[13].

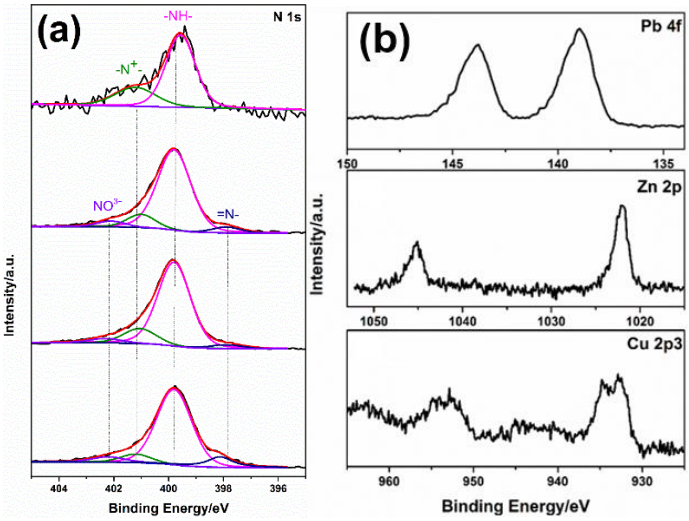


Fig. **1** (a)XPS N 1s core level spectra of the PPy/TiO_2 composite before and after adsorption of Pb^{2+}, Zn^{2+} and Cu^{2+}. (b) Pb 4f, Zn 2p, Cu 2p3 core level spectra of the PPy/TiO_2 composite after adsorption of Pb^{2+}, Zn^{2+} and Cu^{2+}.

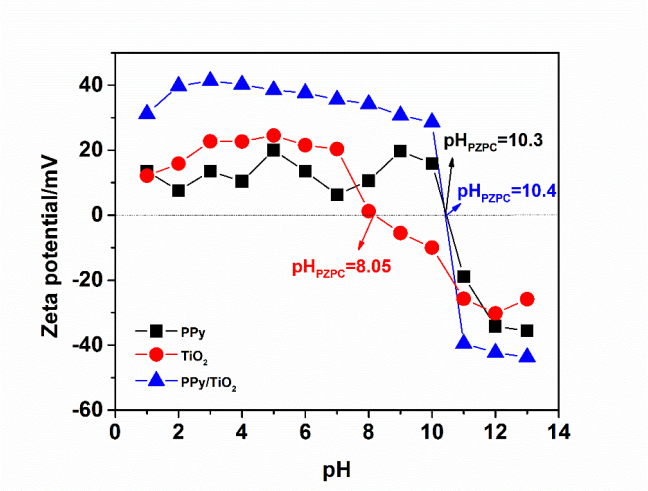


Fig. **2** Zeta potentials of PPy, TiO_2 and the PPy/TiO_2 composite in different pH and their pH of zero-point charge.

The CT interaction is effected by thermal degradation, and the $PPy^+(X^-)$ begins to deprotonate and dedope to DP-PPy (deprotonated-PPy) when it is heated to a certain temperature[24]. Therefore, to further confirm the CT interaction in the composite between TiO_2, PPy and dopant ions ($TiO_2(O^-)$ and SO_4^{2-}), thermogravimetric analysis (TGA) for PPy, TiO_2 and their composite was carried out and shown in Fig. ***S2***. A three-stage process of PPy/TiO_2 in the thermal degradation was observed: the first

weight loss from room temperature to 300 ˚C is assigned to the loss of hydroxyls and physically and chemically adsorbed water [25]; the second weight loss interval between 300 ˚C and 600 ˚C is ascribed to the loss of the doping ions SO_4^{2-}, which agrees with the results from Tan et al. [24] that $PPy^+(Cl^-)$ started to lose the chloride species after having been heated slightly above 300 ˚C; the final weight loss excess above 600 ˚C may be the further thermal decomposition of PPy. This weight loss process is also verified by the proportion loss of each component in the polymer as well as the composite from the TGA result (Table **1**). The mass fraction of SO_4^{2-} in the PPy chain is calculated to be about 18.73 w/w% based on a doping level of 31.2% from the XPS result (for calculation details please see the ***Supporting information***), which fits well with the second weight loss interval of around 19.02 w/w% in the TGA experiment. From the TGA study, more than 70% of the composite is TiO_2, suggesting that the TiO_2 may play a more important role in the adsorption.

Table **1** The proportion of each component in PPy, TiO_2 and the PPy/TiO_2 composite before and after adsorption.

	Temperature		
	<300 ˚C (Water/Hydroxyl)	**300-600 ˚C (Hydroxyl/Doping ions)**	**>600 ˚C (PPy)**
PPy	15.39 w/w% (Water)	19.02 w/w% (Doping ions)	5.80 w/w% (PPy)
TiO_2	14.57 w/w% (Water/Hydroxyl)		-
PPy/TiO_2	12.15 w/w% (Water/Hydroxyl)	7.50 w/w% (Hydroxyl/Doping ions)	4.84 w/w% (PPy)
PPy/TiO_2 Pb	14.17 w/w% (Water/Hydroxyl)	11.38 w/w% (Hydroxyl/Doping ions)	9.06 w/w% (PPy/M^{2+})
PPy/TiO_2 Zn	16.04 w/w% (Water/Hydroxyl)	9.51 w/w% (Hydroxyl/Doping ions)	8.23 w/w% (PPy/M^{2+})
PPy/TiO_2 Cu	16.04 w/w% (Water/Hydroxyl)	9.51 w/w% (Hydroxyl/Doping ions)	4.37 w/w% (PPy/M^{2+})

To better characterize the structure of PPy/TiO_2 composite, the XRD spectra of PPy, TiO_2 and PPy/TiO_2 composite were investigated and depicted in Fig. ***S3***. Amorphous PPy and anatase TiO_2 with

characteristic peaks at 25.3˚, 37.8˚ and 48.1˚ can be confirmed [26]. After being covered with PPy, those three characteristic peaks almost disappeared and showed an amorphous shape, suggesting that the anatase TiO_2 was completely covered by amorphous PPy [27]. This core-shell feature is also supported by the N_2 adsorption-desorption experiment results (Fig. **3**), and the textural parameters were listed in Table ***S2***. The surface area and pore volume of TiO_2 were extensively reduced after modification with PPy, which results from blocking by the PPy, confirming the core-shell structure of PPy/TiO_2 composite. The core-shell structure was also confirmed by the SEM and TEM images shown in Fig. ***S4***. The lattice fringe of TiO_2 can be clearly observed in core of the composite, covered by an amorphous shell of PPy. The pore diameter of the composite is suggested to be around 6.45 nm, which is much larger than the radius of the heavy metal ions (0.97 Å for Pb^{2+}, 0.74 Å for Zn^{2+} and 0.7 Å for Cu^{2+}), indicating that the ions can diffuse through the PPy to the TiO_2 without resistance. It is also interesting to find that the isotherm of TiO_2 was changed from Type II to Type I after PPy modification, further confirming the pore structure changes [28]. Nevertheless, this composite still shows a surface area of 140.0 m^2/g providing sufficient sites for heavy metal adsorption.

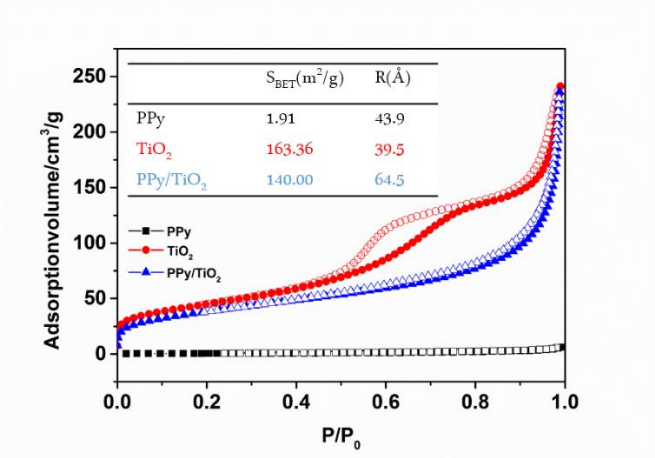


Fig. **3** N_2 adsorption and desorption isotherms of PPy, TiO_2 and the PPy/TiO_2 composite.

3.2 Adsorption investigation

The detailed adsorption properties including kinetic, regeneration investigation and field sample analysis were carried out and are shown in ***Supporting information***. They show that the PPy/TiO_2 composite is a promising adsorbent for adsorption engineering. The adsorption equilibrium can be achieved within 5 min for Zn^{2+}, 7 min for Cu^{2+} and 40 min for Pb^{2+}, showing a novel fast adsorption. It can be recycled using HNO_3 and NaOH, which is low-cost and easily operational. It could also be effectively used in field conditions.

To understand the adsorption properties and selective adsorption nature, and to quantify the maximum adsorption capacity of the PPy/TiO_2 composite, isotherm studies at different temperatures in single and multi-component (ternary) systems were carried out (**Fig. *S*5**)[29]. The equilibrium experimental data are fitted using typical Langmuir [30] and Freundlich [31] models to illuminate the adsorption affinity and capacity, while using Dubinin-Radushkevich [32] and Temkin [33] models to estimate the adsorption free energy and heat. Relevant parameters and details about the models are summarized in **Table 2** and **Table *S*3**. Considering the value of R^2 and the accuracy of the Q_m calculated, the equilibrium data can be well described by the Langmuir model, followed by the Freundlich and Temkin models in all cases, while the Dubinin-Radushkevich model is least able to predict the adsorption. Therefore, the discussions were mainly based on the Langmuir fitting results.

From the Langmuir model, the PPy/TiO_2 composite shows an outstanding maximum adsorption capacity up to 0.677 mmol/g for Pb^{2+}, 1.197 mmol/g for Zn^{2+} and 0.141 mmol/g for Cu^{2+}, respectively in single ion solutions. Moreover, it is noticeable that the Q_m in the Pb^{2+} and Zn^{2+} adsorption spectra increases steadily with temperature, which may result from the ionic exchange adsorption nature[20].

This phenomenon was also reported for other PPy-based adsorbents such as a PPy/chitin composite that adsorbed Pb^{2+} and Cd^{2+}[34] and a PPy/sawdust composite used for Zn^{2+} adsorption[35]. In contrast, the temperature did not obviously influence the Cu^{2+} adsorption. In this case, the adsorption of Cu^{2+} may have a different adsorption mechanism than Pb^{2+} and Zn^{2+}.

Table **2** Single and multi-component adsorption isotherms parameters describing the adsorption of heavy metals (Pb^{2+}, Zn^{2+}, Cu^{2+}) onto PPy/TiO_2 composite, based on the Langmuir and Freundlich models.

			Samples														
			PPy/TiO_2									**PPy**			**TiO_2**		
			Pb			**Zn**			**Cu**			**Pb**	**Zn**	**Cu**	**Pb**	**Zn**	**Cu**
			15˚C	**25˚C**	**45˚C**	**15˚C**	**25˚C**	**45˚C**	**15˚C**	**25˚C**	**45˚C**	**25˚C**	**25˚C**	**25˚C**	**25˚C**	**25˚C**	**25˚C**
Langmuir	**Single**	$Q_{m,mass}$	125.79	140.27	237.03	72.65	77.81	83.88	10.32	9.01	9.27	65.27	67.51	40.50	68.13	46.83	15.63
		$Q_{m,mol}$	0.607	0.677	1.145	1.117	1.197	1.29	0.160	0.141	0.145	0.315	1.039	0.633	0.329	0.720	0.244
		K_L	0.0061	0.0046	0.0022	0.0058	0.0068	0.0078	0.0044	0.0073	0.013	0.0017	0.0045	0.0019	0.020	0.0029	0.0010
		R^2	0.996	0.997	0.991	0.996	0.995	0.994	0.997	0.995	0.991	0.991	0.995	0.998	0.980	0.994	0.997
	Multiple	$Q_{m,mass}$	-	65.52	-	-	40.38	-	-	0	-	122.06	125.18	124.79	45.38	45.12	0
		$Q_{m,mol}$	-	0.312	-	-	0.621	-	-	0	-	0.0583	1.926	1.950	0.219	0.694	0
		K_L	-	0.01746	-	-	0.00046	-	-	-	-	0.014	0.019	0.015	0.0039	0.0022	-
		R^2	-	0.994	-	-	0.988	-	-	-	-	0.978	0.993	0.991	0.998	0.999	-
		P		**0.467**			**0.519**			**0**		**0.184**	**1.854**	**3.081**	**0.666**	**0.963**	**0**
Freundlich	**Single**	K_F	6.91	5.00	2.23	2.28	2.85	3.52	0.27	0.47	0.98	0.98	2.10	0.504	16.66	0.58	0.10
		$1/n$	0.42	0.48	0.65	0.52	0.50	0.49	0.52	0.44	0.34	0.65	0.57	0.71	0.21	0.62	0.80
		R^2	0.998	0.998	0.963	0.989	0.982	0.986	0.988	0.981	0.922	0.968	0.966	0.989	0.744	0.971	0.790
	Multiple	K_F	-	6.45	-	-	0.148	-	-	-	-	12.37	17.23	13.63	1.15	0.30	-
		$1/n$	-	0.39	-	-	0.94	-	-	-	-	0.38	0.32	0.35	0.64	0.72	-
		R^2	-	0.941	-	-	0.979	-	-	-	-	0.994	0.891	0.917	0.995	0.997	-

Langmuir model: $Q_e = \frac{Q_m K_L C_e}{1+K_L C_e}$, $P = \frac{Q_{max,single}}{Q_{max,multiple}}$.

Q_e (mg/g)is the adsorption capacity; $Q_{m,mass}$ (mg/g)/$Q_{m,mol}$ (mmol/g) represents the maximum adsorption capacity; K_L (L/mg) is an Langmuir constant relate to the affinity between adsorbents and adsorbate; P factor is a dimensionless parameter to estimate the selectivity for heavy metals.

Freundlich model: $Q_e = K_F C_e^{1/n}$.

K_F($mg^{1-n} \cdot L^n/g$) is a constant related to the adsorption capacity of adsorbent when the equilibrium metal ions concentration equals to 1; n states the degree of dependence of the adsorption on the equilibrium concentration.

The multiple ion solution was applied to further investigate the selective adsorption property of PPy/TiO_2 composite, which is important in adsorption engineering but is rarely reported. The Langmuir model still describes the adsorption data best, indicating that the multi-adsorption is still monolayer. It is reasonable that the adsorption capacities (Q_m) deteriorate to some extent due to the competition between heavy metals for the adsorption sites. To better correlate the data obtained from single metal equilibrium with the multi-metal data, the ***P*** factor, which is a dimensionless parameter shown in **Eq. (3)**, is introduced.

$$\boldsymbol{P} = \frac{Q_{max,single}}{Q_{max,multiple}} \quad (3)$$

Where, $Q_{max,single}$ and $Q_{max,multiple}$ are the maximum adsorption capacity of heavy metals in single and multi-component systems. Obviously, the higher the affinity towards one metal, the higher the value of ***P*** is; and the better the selectivity the composite has, the bigger the difference in the ***P*** values is for different metal ions. The ***P*** values of the composite for three heavy metals are also recorded in Table **2**. It is interesting to see that the ***P*** values show a descending order of Zn^{2+}>Pb^{2+}>>Cu^{2+}, and the adsorption of Cu^{2+} is almost completely forbidden in the multi-component system, suggesting that the PPy/TiO_2 composite can be applied to separate and recycle heavy metals from Cu^{2+} rich electroplating effluent without the influence and competition of Cu^{2+}. It should be noted that there is not a mechanism about selective adsorption that can perfectly explain all the experimental results yet, and the reported results contradict with each other in reported literature. For example, Z.J. Xu et al. [36] reported the selective adsorption of heavy metals to be in the order of Cu(II) > Co(II) > Ni(II) for a SG-H_2L^2 composite, and they suggested that it may be caused by other factors involved in the adsorption process, such as the cationic radius, hydration energy and acidity/basicity of the interactive species. However, contradicting results were observed by J. Ali et al.[37] who suggested the selective adsorption order of a

Mn-MoS_4 composite followed the order Hg(II) > Ag(I) > Pb(II) > Cu(II) > Cd(II) > Ni(II) > Zn(II) > Co(II), in which the mechanism of selectivity is based on the Hard-Soft-Acid-Base theory. In addition, Ag(I), which carries only one positive charge, outperforms other ions which have greater charges, challenging the theory that the more charged ions would have higher adsorption priority. Another differing result was reported of a PPy/TiO_2 composite that had selective adsorption in the order Zn^{2+}>Pb^{2+}>>Cu^{2+} ,even though Zn^{2+} has a smaller ionic radii and Pauling electronegativity (0.74 nm and 1.65, respectively) than Pb^{2+} (0.97 nm and 2.33, respectively) and Cu^{2+} (0.7 nm and 1.9, respectively), suggesting that the selectivity of the adsorbent majorly depends on both of the adsorbent and adsorbate, and the mechanism proposed before cannot well explain all these situations.

In order to know more about the selectivity of the PPy/TiO_2 composite, competitive adsorption studies of PPy and TiO_2 was also conducted, which were summarized in **Fig. *S*5 (d-i)** and Table **2**. It is interesting to notice that that TiO_2 showed a similar adsorption behavior in a multi-component system to the PPy/TiO_2 composite. Such behavior was not observed for PPy. In addition, TiO_2 did show a similar selectivity order to that of PPy/TiO_2, which follows Zn^{2+}> Pb^{2+}> Cu^{2+}. Therefore, it can be deduced that the selectivity for heavy metals for this composite was determined by TiO_2 instead of PPy. It can be hypothesized that Pb^{2+} and Zn^{2+} are favored by TiO_2, while Cu^{2+} is not favored by TiO_2 and the PPy/TiO_2 composite, even though PPy has a good affinity towards Cu^{2+}. Cu^{2+}can be only adsorbed by the PPy by the limited imine groups. Despite the prior information, the reason why a metal oxide would have special affinity towards specific heavy metal ions could not be given. However, inspired by the work conducted by O.A. Oyetade et al. [38], who conducted DFT calculations to simulate the combination of ions with acid functionalized multiwalled carbon nanotubes on a lattice structure

scale, we hypothesize herein that the selectivity of the metal oxide to heavy metal ions should relate to the compatibility for the lattice structures of metal oxides and heavy metal ion hydroxide. The further investigation in this area will be in the subject of our future work.

From the fitting results of the Dubinin-Radushkevich and the Temkin model, it can be seen in Fig. ***S*6-*S*7** and **Table *S*3** that the adsorption free energy (***E***) and heat (***B***) also follow the increasing trend with the temperature, which is consistent with the results from the Langmuir model. However, these two models cannot describe the data well, therefore the value of the adsorption free energy (***E***) and heat (***B***) are not used to determine the adsorption mechanism.

3.3 Synergistic adsorption and selective adsorption mechanism

Inspired by the interesting selective adsorption properties of the PPy/TiO_2 composite, we continued to design and carry out experiments to investigate the mechanism of the synergistic adsorption between PPy and TiO_2, and the selective adsorption mechanism for heavy metals.

3.3.1 Adsorption sites

FT-IR analysis before and after heavy metal adsorption for TiO_2, PPy and the PPy/TiO_2 composite were performed (Fig.***S*1(b-d))** to determine the adsorption sites, and the main characteristic peaks were listed in Table ***S*1**. For TiO_2, the peaks assigned to the hydroxyls at 3419 cm^{-1} and 1629 cm^{-1} showed an obvious red shift to higher wavenumbers after adsorbing Pb^{2+}, Zn^{2+} and Cu^{2+}, suggesting an interaction between the hydroxyls on the surface of TiO_2 and heavy metals after dedoping[39]. The peak shift of Cu^{2+} was relatively smaller than the other two ions, confirming the result obtained by the competitive isotherm investigation that adsorption of Cu^{2+} is not favorable for TiO_2. As for PPy and

the PPy/TiO_2 composite, a red shift was clearly observed for the peak ascribed to C-N situated at around 1442 cm^{-1} as well, and its intensity became very weak after adsorption, indicating a new environment around the pyrrolylium nitrogen on the PPy chain [24]. This result may be one of the important evidences for the ionic exchange and dedoping of $TiO_2(O^-)$ during adsorption.

3.3.2 Synergistic adsorption and selective adsorption mechanism

It is difficult to interpret the selective adsorption order of Zn^{2+}> Pb^{2+}>> Cu^{2+} for the PPy/TiO_2 composite if using the Hard-Soft-Acid-Base theory or the properties of heavy metals only. Therefore, the synergistic adsorption between TiO_2 and PPy in the selective adsorption process was also considered. As we discussed above, the $TiO_2(O^-)$ together with SO_4^{2-} acts as a dopant and is involved in the charge-transfer interaction with PPy in the PPy/TiO_2 composite. However, the unstable oxidization doped state of PPy is relatively easy to dedope or to exchange dopants with rich ions such as NO_3^- in the heavy metal ion solution at pH>3 [40], and some imine could be formed. To illuminate this process, XPS investigations on the composite after adsorption was conducted. The N1s spectra of PPy/TiO_2 after adsorption are depicted in Fig.**1**, and the assignments and their ratio of peak area are presented in Table **3** to illustrate the change of N nature. It shows an interesting result: a decreased ratio of -N^+-, an increased ratio of =N-, and an unchanged ratio of -NH-; confirming a certain degree of dedoping for the composite. However, the TGA results shown in Table **1** infer that the mass of doping ions (300-600 ˚C) still increased after adsorption, suggesting that the dedoped ions should be the $TiO_2(O^-)$ instead of SO_4^{2-}; some $TiO_2(O^-)$ may be also exchanged by NO_3^- doping into PPy chain[24]. It is reasonable because the SO_4^{2-} has a large size and is relatively hard to dedope from the PPy chain. From the XPS result, another interesting result can be also noticed is that for Pb^{2+} and Zn^{2+}, which are

favorable by PPy/TiO_2, the dedoping rate is much lower (larger A($-N^+-$)/A(=N-)) than for Cu^{2+}, which is unfavorable. It can be inferred from this result that Cu^{2+} may be mostly adsorbed on PPy, in a different manner than Pb^{2+} and Zn^{2+}. This is due to the chemical equilibrium between the metal ion and PPy, where the dedoping process can be promoted by heavy metal ions if heavy metal ions have an interaction with PPy as follows:

$$PPy(-N^+-)X^- == PPy(=N-) + HX \quad (4)$$

$$PPy(=N-) + Cu^{2+} == PPy(=N-)Cu^{2+}. \quad (5)$$

This reaction can be also confirmed by the XPS spectra of Cu 2p, in which the Cu-N can be obviously detected after adsorption (Fig. **1(b)**), suggesting the main adsorption site for Cu^{2+} is on the PPy through the imine. The similar shape line is also found in Cu/N doped TiO_2[41]. As for Pb^{2+} and Zn^{2+}, the peaks for Pb-N and Zn-N are overlapped and only hydrated (Pb-O and Zn-O) and nitrated forms can be detected [42, 43], confirming that Zn^{2+} and Pb^{2+} were mainly adsorbed on TiO_2 while Cu^{2+} was adsorbed by PPy on the imine group, which further supports the hypothesis that Zn^{2+} and Pb^{2+} are more favorable by TiO_2. From the XPS result, it can also be seen that the oxidation rate of PPy after adsorption decreases to around 20%, which is attributed by the hydrolysis in the non-acid aqueous solution.

Table **3** The assignment and ratio of peak areas in the XPS N 1s core level spectra of the PPy/TiO_2 composite after Pb^{2+}, Zn^{2+} and Cu^{2+} adsorption (the FWHM is set as 1.4 eV, and the %Lorentzian-Gaussian is set as 20%).

	Pb			Zn			Cu		
Assignment[16]	Binding energy/eV	Ratio of peak area	A(-N^+-)/A(=N-)	Binding energy/eV	Ratio of peak area	A(-N^+-)/A(=N-)	Binding energy/eV	Ratio of peak area	A(-N^+-)/A(=N-)
=N-	397.87	4.869%	2.264	397.97	4.176%	3.971	398.17	7.668%	0.771
-NH-	399.77	79.269%		399.77	78.168%		399.77	76.534%	
-N^+-	400.97	11.001%		401.07	14.104%		401.27	5.856%	
NO_3^-	402.07	4.861%		402.27	3.552%		402.17	9.942%	

Taking the above into consideration, we summarize and propose the mechanism on the synergistic adsorption for PPy/TiO_2 composite for the first time as follows: $TiO_2(O^-)$ together with SO_4^{2-} is suggested as the dopants for the PPy and is involved in charge-transfer interactions with PPy in the PPy/TiO_2 system. After the composite is dosed with the heavy metal solution at pH greater than 3, the exchange/dedoping process of dopants can occur. A part of $TiO_2(O^-)$ would be dedoped and exchanged by the counter-anions in the solution (here is NO_3^-) due to the high concentration of rich NO_3^- in the solution[44]. After being dedoped, the negatively charged $TiO_2(O^-)$ needs to be electrically neutralized. In solutions at pH=5, heavy metal ions would be preferentially attracted to $TiO_2(O^-)$ for electroneutrality. Thus, the selective adsorption is mainly achieved at the TiO_2, resulting in the interesting phenomenon that the selectivity of the composite is determined by the interaction between TiO_2 and heavy metal ions instead of PPy. Therefore, the PPy/TiO_2 composite has better affinity to Zn^{2+} and Pb^{2+} than Cu^{2+}, just as TiO_2 does. In other words, the novel selectivity is achieved through the synergistic adsorption between PPy and TiO_2. For the adsorption mechanism, according to R. Zare-Dorabei and our previous work, hydroxyls become negatively charged after dedoping from PPy, resulting in the adsorption of heavy metal ions with positive charge through the electrostatic attraction. Therefore, the electrostatic attraction would be an important mechanism for the adsorption. In addition, for the pyrrolylium nitrogen which has lone pair electron in the PPy, the chelation of nitrogen to the heavy metal ions with unoccupied orbital could be another important mechanism for the adsorption after dedoping. The adsorption mechanism could be expressed as follows:

2Composite-O^- (hydroxyl)+ M^{2+} (heavy metal ion) → 2Composite-O^---M^{2+} (electrostatic attraction) (6)

Composite-N: (pyrrolylium nitrogen)+ M^{2+} (heavy metal ion) → Composite-N: → M^{2+} (chelation) (7)

It should be noted that even though the PPy has adsorption capacity to heavy metals through chelation, however, the loading of PPy is low compared to TiO_2 from TGA result. Therefore, the selective adsorption property is still determined by TiO_2.

We conducted the experiments by adjusting the solution pH (depicted in Fig. ***S*8**) to confirm this synergistic mechanism. The adsorption capacities for Pb^{2+}, Zn^{2+} and Cu^{2+} increased with the increased pH. This result supports the synergistic mechanism we proposed because when the composite is dosed into the solution with higher pH, the dedoping of the dopant and the dopant exchange would be greatly improved due to the low concentration of H^+, resulting in the available of the $TiO_2(O^-)$ adsorption site and enhancement of the adsorption capacity for heavy metal ions [24]. In addition, the amount of imine group could be also increased at high pH, which may also increase the adsorption capacity[27].

4. Conclusion

The investigation on the mechanism of the synergistic adsorption between polymer and metal oxide is an important issue for the adsorbent design and application. Herein, the mechanism on the synergistic adsorption between polymer and metal oxide in a polymer/metal oxide composite was discovered and proposed for the first time, and the self-doping nature of metal oxide on polymer was carefully illuminated. The PPy in its oxidized p-type doping state with 31.2% doping degree is coated on the surface of the TiO_2 which is in the n-type state, forming an interesting charge-transfer structure. This interaction results in the interesting selective adsorption property that Zn^{2+} can be selectively adsorbed with 77.81 mg/g adsorption capacity while the adsorption for Cu^{2+} was totally suppressed in a multiple

heavy metal ion solution. The XPS, TGA and FTIR were applied for the mechanism investigation. The results show peak shifts assigned to hydroxyls and pyrrolylium nitrogen in FTIR, a decreased ratio of $-N^+-$, an increased ratio of =N-, and an unchanged ratio of -NH- in XPS, and weight loss ascribed to doping ions in TGA, confirming a certain degree of dedoping for the composite, and the exchange/dedoping of $TiO_2(O^-)$ occurred during the adsorption process. It further results in the interesting phenomenon that the selectivity of the composite was determined by the TiO_2. This mechanism we proposed herein satisfactorily explains the interesting properties of synergistic adsorption and selective adsorption in this system. It may also be suitable in other polymer/metal oxide composites whose polymer can conduct the doping-dedoping process, such as polythiophene and polyaniline, and gives a guideline to get insight into the mechanism on the selective adsorption in other adsorbents. With this guideline, the heavy metal ions can be recycled with higher efficiency and lower cost compared to other treatment method. However, the Pb^{2+} and Zn^{2+} cannot be separated by PPy/TiO_2. Meanwhile, the reason why the TiO_2 has special adsorption affinity to Zn^{2+} and poor affinity to Cu^{2+} remains unknown. We hypothesize herein that the selectivity of the metal oxide to heavy metal ions should relate to the compatibility for the lattice structures of metal oxides and heavy metal ion hydroxide. The further investigation will be conducted in our future work in this case.

ASSOCIATED CONTENT

Supporting information

Additional figures: FTIR spectra of PPy, TiO_2 and the PPy/TiO_2 composite before and after Pb^{2+}, Zn^{2+} and Cu^{2+} adsorption; TGA analysis of PPy, TiO_2 and the PPy/TiO_2 composite before and after adsorption of Pb^{2+}, Zn^{2+} and Cu^{2+}; XRD spectra of PPy, TiO_2 and the PPy/TiO_2 composite; SEM and

TEM images of the PPy/TiO_2 composite; Single and multi-component adsorption isotherms for the adsorption of heavy metals onto the PPy/TiO_2 composite, PPy and TiO_2, fitting with Langmuir model, Freundlich model, linear form of Dubinin-Radushkevich model and Temkin model; The adsorption capacities of the PPy/TiO_2 composite for Pb^{2+}, Zn^{2+} and Cu^{2+} in different initial pH.

Additional table: Assignments of the FT-IR absorptions for PPy, TiO_2 and the PPy/TiO_2 composite before and after adsorption of Pb^{2+}, Zn^{2+} and Cu^{2+}; The textural properties of PPy, TiO_2 and the PPy/TiO_2 composite before and after adsorption; Single and multi-component adsorption isotherms parameters describing the adsorption of heavy metals (Pb^{2+}, Zn^{2+}, Cu^{2+}) onto the PPy/TiO_2 composite, based on Dubinin-Radushkevich and Temkin models.

Additional scheme: Interconversions between the various redox states in PPy.

Additional experiments and discussion: Calculation for the amount of SO_4^{2-} in the PPy chain; Kinetic investigation; Regeneration; Field sample analysis.

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